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Prediction of raspberries puree quality traits by Fourier transform infrared spectroscopy

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ABSTRACT

FTIR applications combined with chemometric methods can provide alternative techniques to conventional methods to determine quality traits of fruits or vegetables. In the present study, these techniques were used to predict the main traits involved in sensory quality of raspberry fruits (such as soluble solids content, total acid, pH, fructose, glucose and sucrose) and the main bioactive compounds implied in antioxidant capacities (vitamin C, phenolics and anthocyanins). Partial Least Squares regressions (PLS) were used to develop the prediction models. A leave-one-out procedure has been performed to determine the optimal number of latent variables and the wavenumber selection; and k-one-out procedure (2/3, 1/3) to calibrate and to cross-validate the models. Excellent predictions were achieved for quality traits (pH, TA, SSC) with R^2-greater than 0.90, except for TA prediction in the second validation steps where R^2-value decreased to 0.61. Predictions of reducing sugars and sucrose were also excellent with R^2-values above 0.95 in both validation steps. Models aiming at to predict bioactive compounds presented lower performances than sugar models. They remain acceptable and promising for vitamin C and phenolics ($R^2 \geq 0.65$; RMSECV $\leq$ 12%). Finally, the validation of anthocyanins prediction model did not give satisfactory results.

1. Introduction

Since the interest of bioactive compounds and their bioavailability in fruits and vegetable are increasing for the consumers, many current studies focus on their quantification and qualification. Among these products, raspberries are a part of the most appreciable fruits due to their taste and their well-known high level of health related compounds with high antioxidant activities (Rao & Snyder, 2010). Its sweet flavor is especially related to the concentration of fructose, glucose and sucrose, the two first ones with a higher levels (Kafkas, Özgen, Özogui, & Turemis, 2008); whereas the beneficial compounds are mainly due to the action of Vitamin C and the high polyphenol contents. However, the analysis of these compounds by the different conventional methods is generally time consuming and expensive because of the many chemicals and skilled labor they require.

Recently, many studies paid particular attention to the possibility of measuring quality traits of various food products by FTIR spectroscopy. The interest for this method is essentially due to the rapidity of the method, the possibility of determining several quality traits simultaneously and the ease of implementation. Several studies aiming to determine fruits composition by FTIR spectrometry were published in order to make this tool available as an application in food-processing area. Bureau et al. (2009) have developed accurate FTIR methods to determine sugars and organic acids in apricot fruits ($R^2 \geq 0.74$ SEP $\leq$ 18%). Lam, Proctor, Howard, and Cho (2005) reported good correlations between blueberry, grape and blackberry antioxidant capacity values and FTIR estimates ($R^2 \geq 0.87$, SEC $\approx$ 5%). Regarding the processed fruit products and by quoting only the most recent studies, Queji, Wosiacki, Cordeiro, Peralta-Zamora, and Nagata (2010)showed the usefulness of FTIR to determine simple sugars, malic acid and phenolic compounds in apple pomace samples ($0.86 \leq R \leq 0.99$). With the

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red wine, Versari, Parpinello, Scazzina, and Rio (2010) predicted total antioxidant capacity values (R = 0.85, SEP = 4.7) and Laghi, Versari, Parpinello, Nakaji, and Boulton (2011) the total wine color, anthocyanins and polymeric pigments ($R^2 \geq 0.82$, SEP $\leq$ 0.9). Finally, Cerretani et al. (2010) determined water and phenolic contents of olive oil with a satisfactory limit of detection. This technique is also used in other applications such as the detection of adulteration or fermentation of derivative products (Di Egidio, Sinelli, Giovanelli, Moles, & Casiraghi, 2010; Kemsley, Holland, Defernez, & Wilson, 1996).

Nevertheless, FTIR results for each new biological matrix could vary due the complexity and the numerous nutrients constituting the material to be analyzed. In this study, FTIR coupled with appropriated data processing could be particularly interesting in the framework of varietal selection programs. Especially as the interest of the market for high quality raspberries continues to increase, obliging an improvement of the quality of raspberries at the production level. A rapid and easy assessment of the fruit quality traits and their health related compounds would be helpful to select the most promising cultivars for the producers but also for the consumers who are more and more aware on the food composition.

Therefore, the objective of this research was to apply FTIR spectroscopy, coupled with the appropriate chemometric methods, to predict first the main quality traits of raspberry fruits and second the main bioactive compounds implied in antioxidant capacity. For quality traits pH, titratable acidity, soluble solids content and individual sugars were measured. For the bioactive compounds with a health benefit, the predictions were focused on vitamin C, total polyphenol and total anthocyanin contents.

2. Materials and methods

2.1. Raspberries samples

Fruits collected for this work were harvested in 2011 from the experimental trials conducted in Conthey, Switzerland (Agroscope, Centre de Recherche Conthey). Eight floricane fruiting cultivars ('Cascade Delight', 'Elida', 'Eva', 'Glen Ample', 'Meeker', 'Tulamagic', 'Tulameen' and 'Willamette') and six primocane fruiting cultivars ('Autumn Bliss', 'Joan J.', 'Erika', 'Heritage', 'Himbo Top', 'Polka' and 'Sugana') were selected with 3 replications per cultivar and 8 plants per replication. Moreover, two fruit batches corresponding to the cultivar 'Polka', respectively cultivated in Bulgaria and Slovenia, were added to the analysis of the present study. Raspberries were collected at the peak of the harvest period according the concerned cultivars and immediately frozen and stored at −20 °C until analysis.

The calibration and the first validation were performed with fruits that were frozen at −20 °C for a few days from harvest to the time of chemical and FTIR analyses. For the second validation, the fruit were stored at −20 °C for about one year prior to the chemical and FTIR analyses.

2.2. Sample preparation

Raspberries were defrosted and homogenous aliquots of each cultivar were homogenized in an A10 IKA blender (Janke & Kunkel AG, Staufen i.Br., D), resulting in a puree containing intact seeds. This puree was diluted with water 1:1, centrifuged at 3500 g for 15 min. The supernatant was filtered through a Whatman filter paper (No. 595.5) and the resulting filtrate (further referred to as aqueous extract) was used to measure pH, titratable acid, soluble solids and individual sugars as well as to record FTIR spectra. To determine vitamin C, 3 g of the above mentioned puree were extracted with 50 ml of a KH_2PO_4 buffer (0.2 mol/L, pH 5.0) containing 0.1 g/100 ml dithiothreitol, sonicated for 15 min and kept in the dark at room temperature for 2 h. After centrifugation at 3500 × g for 15 min, an aliquot was filtered through a 0.45 μm nylon filter and immediately analyzed by HPLC. Total phenolics and total anthocyanins were quantified in methanolic extracts. For that, 20 ml of pure methanol were added to 5 g of the above mentioned puree, mixed and sonicated for 15 min. The volume was adjusted to 25 ml with 80 ml/100 ml of methanol and the samples were centrifuged at 3500 × g for 15 min. Supernatants were collected and stored at −80 °C until analysis.

2.3. Analytical analyses

Soluble solids content (SSC), expressed in °Brix, were analyzed in the aqueous extracts with a digital refractometer (Atago, PR-1, Kunzmann). pH was measured and 5 g of this aqueous extract was titrated with 0.1 N NaOH to pH 8.1. Titratable acid was expressed as g malic acid equivalent per 100 g of fresh weight (fw) according to Weber, Perkins-Veazie, Moore, and Howard (2008) methods. Quantification of individual sugars was performed on a Konelab Arena 20XT analyzer (Thermo Fisher Scientific OY, Vantaa, FI) by using enzymatic methods. Aqueous extracts were diluted 1:40 and analyzed by applying test kits (E5120 Enzytec Fluid D-Fructose, E5140 Enzytec Fluid D-Glucose und E5180 Enzytec Fluid Sucrose; R-Biopharm, Darmstadt, D). Absorbance was measured at 340 nm and contents of fructose, glucose and sucrose were respectively quantified by using external calibration curves. The results were expressed in g/100 g of fw.

Vitamin C was determined by HPLC-UV according to Crespo, Bordonaba, Terry, and Carlen (2010) on a RP18 column (Nucleodur 100-5, 4 × 250 mm, Macherey–Nagel, Oensingen, CH) and using KH_2PO_4 buffer as mobile phase. Absorbance was measured at 254 nm. Vitamin C was quantified by using an external calibration curve and results were expressed in mg per 100 g of fw. Quantification of total phenolics content was performed by the Folin Ciocalteu assay on the Konelab Arena 20XT analyzer. For that, 10 μl of fivefold diluted methanolic extract were mixed with 40 μl of Folin-Ciocalteu's phenol reagent (Merk AG, Zug, CH), followed by adding 40 μl of sodium carbonate solution at 200 gL^{-1}. After 30 min of incubation at 37 °C, absorbance was measured at 700 nm (Anttonen & Karjalainen, 2005). Total phenol content was calculated as mg of gallic acid equivalent (GAE) per 100 g of fw. Total anthocyanin content was determined by the pH differential method (Lee, Rennaker, & Wrolstad, 2008), adapted to the Konelab Arena 20XT analyzer. 5 μl of undiluted methanolic extract was mixed with buffer pH 1.0, incubated for 1 min at 37 °C and absorbance was measured at 520 nm. 42 μl of pH buffer of 4.5 were added, incubated for 2 min at 37 °C and absorbance was recorded at 700 nm. Total anthocyanin content was calculated by means of the extinction difference and expressed as mg cyanidin-3-glucoside equivalents (C3GE) per 100 g of fw.

2.4. FTIR analysis

FTIR spectra of aqueous extracts were recorded by means of a WineScan FT120 interferometer (Foss Tecator, Germany). For each sample a total volume of 30 ml was used to rinse the device between samples and to record spectra from 5020 cm^{-1} to 925 cm^{-1} at a resolution of 4 cm^{-1} by pumping the sample through a CaF_2-lined cuvette with an optical path length of 37 μm. Each sample was scanned in triplicate and analysis was performed at 40 °C (Baumgartner, Bill, & Roth, 2001). After a series of 6 samples the spectrometer was cleaned with the Cleaning Agent S-470 (Foss Analytical, Denmark) and zeroed by means of the Zero solution S-6060 (Foss Analytical, Denmark).